NASA TM-86283

NASA Technical Memorandum 86283

A STUDY OF THE EFFECTS OF END-CAP MOLECULAR SPECIES ON ENVIRONMENTAL CHARACTERISTICS OF POLYIMIDESULFONES

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AUGUST 1984

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SUMMARY

Polyimidesulfone ($PISO_2$) is a promising polymer developed at Langley. In a continuing effort to further improve its environmental stability and mechanical properties, we decided to investigate the effects of various types of end-caps on its thermo-mechanical and related properties. It is noted that end caps are effective in reducing the environmental damage susceptibility of $PISO_2$ samples, apparently due to their ability to react with free end groups which are believed to be moisture pickup sites. Phthalic anhydride, aniline and aminobenzophenone were the end caps used in this study.

INTRODUCTION

Polyimidesulfone ($PISO_2$) is a very promising, high temperature polymer developed at Langley[1,2]. It is a candidate for several aerospace applications. For this reason it would be highly desirable if its environmental stability could be further enhanced. $PISO_2$ is a linear aromatic polymer which may contain free amine and anhydride or acid end groups. These end groups are believed to be moisture pickup sites. The end groups may be modified by the introduction of appropriate end caps in the $PISO_2$ chain. We have investigated the effects of phthalic anhydride, aniline and 4- aminobenzophenone end caps on the thermo-mechanical and related properties of $PISO_2$ samples. Results of these measurements are described in the following sections. Also discussed are the results of positron annihilation studies conducted in the variously end-capped $PISO_2$ specimens.

EXPERIMENTAL RESULTS

A polyimidesulfone molecular chain is characterized by an equal number of amine and anhydride chemical groups to form imide moieties. Figure 1 shows a molecular chain arrangement for $PISO_2$ polymer. In the present study, various concentrations of phthalic anhydride, aniline and aminobenzophenone were introduced into the $PISO_2$ chain during its preparation. Moldings in the forms of 1" dia. x 0.1" discs were made from each mixture. Measurements of thermochemical properties and free volumes were made for each specimen.

1. $PISO_2$ With Phthalic Anhydride Caps: Figure 2 shows a $PISO_2$ chain with phthalic anhydride caps. The phthalic anhydride (PA) concentration was varied from 0 to 3% and thermochemical properties of the specimens were measured for each concentration. The results are summarized in Table I. Table II summarizes the saturation moisture contents of these specimens as a function of their PA end-cap

concentration. It is apparent that the introduction of PA end-caps makes the specimens more moisture resistant. It may be partly due to the fact that the PA's neutralize the amine ends in $PISO_2$ which are believed to be a moisture pickup site. In order to shed some light on this issue, positron lifetime measurements were made in $PISO_2$ samples containing 0% PA end caps and 3% PA end caps. The results are summarized in Table III. It is apparent that the presence of PA end caps interferes with the normal entry of H_2O molecules into the $PISO_2$ polymeric chain.

2. $PISO_2$ With Aniline Caps: Figure 3 shows a $PISO_2$ chain with aniline caps. Aniline is expected to eliminate the acids or anhydrides that are residual in the polymer. Aniline concentration was varied from 0 to 3%. The saturation moisture contents of aniline-capped $PISO_2$ specimens are summarized in Table IV. Apparently, the saturation moisture content is independent of the aniline end-cap concentration beyond 2%.

3. $PISO_2$ With Aminobenzophenone Caps: Figure 4 shows a $PISO_2$ chain with aminobenzophenone (ABP) caps. Like aniline, aminobenzophenone is also expected to tie up residual acid or anhydride groups. The ABP end-cap concentration was varied from 0 to 3%. The saturation moisture content values were measured in all these specimens. The results are summarized in Table V. Again, like aniline end caps, the maximum effect of ABP end caps on saturation moisture content is realized at very low concentrations.

Since aniline and ABP end caps have similar effects on saturation moisture contents in $PISO_2$ samples, β^+-annihilation measurements were confined only to specimens containing 3% aniline and 3% ABP. The β^+-annihilation data in $PISO_2$ samples endcapped with 3% of PA, aniline and ABP are summarized in Table VI.

4. Effect of PA Caps on Adhesive Properties: The effect of endcapping the $PISO_2$ with varying concentrations of phthalic anhydride on its adhesive properties was also studied. Titanium (6-Al, 4-V) lap shear samples were prepared and tested according to ASTM D1002. The surface of the titanium adherends was lightly grit-blasted and cleaned with an alkaline solution. This was followed by the formation of a stable oxide layer on the surface by treating with a commercially available mixture of chromic and hydrofluorosilicic acids (PASA JELL 107 from SEMCO in Glendale, California). The specimens were bonded using adhesive scrims which had been prepared from 0%, 0.5% and 1% endcapped versions of the $PISO_2$. These scrims had been pretreated to 200°C to ensure imidization and loss of solvent. The specimens were bonded by heating the overlapped adherends with the scrim in the bondline to 335°C under 200 psi. The samples were allowed to cool to 150°C before removal from the bonding fixture.

Although there were differences in initial strengths which correlated to a loss in strength with increasing endcap concentration, the strengths after a 72-hour water boil were quite similar. This might imply that the free amine end groups aid in adhesion or that the lower molecular weight of the endcapped systems causes a lowering of strength. However, the endcapped systems did perform better on a comparative percentage loss basis when they were exposed to moisture (Table VII).

CONCLUSIONS

A novel polyimidesulfone polymer was prepared with various types of end caps in order to assess their effect on moisture pickup in the polymer. It was found that the use of phthalic anhydride as an endcapping agent led to significantly improved moisture resistance. The improvement in moisture resistance was proportional to the molar percentage of phthalic anhydride. Aromatic amines, such as aniline and 4-aminobenzophenone, as end caps appear to saturate at very low concentrations (< 2% for aniline and < 0.5% for ABP). From this work it may be concluded that the free end groups,which are present in the polyimidesulfone,are a major factor in determining its moisture uptake. These units can be chemically eliminated by the addition of suitable endcapping agents. An adhesive study showed that phthalic endcapped polyimidesulfone had less percentage strength loss after a water-boil exposure than did the unendcapped system.

REFERENCES

1. St. Clair, Terry L. and Yamaki, David A.: A Thermoplastic Polyimidesulfone, NASA Technical Memorandum 84574, November 1982.

2. Singh, Jag J.; St. Clair, Terry L.; Holt, William H.; and Mock, Willis, Jr.: Positron Lifetime Studies in Thermoplastic Polyimide Test Specimens, NASA Technical Memorandum 84532, July 1982.

Table I. Summary of Properties of $PISO_2$ Specimen With Phthalic Anhydride (PA) End Caps*

PA Concentration (%)	MW (amu)	Tg (^oC)	Repeat Unit, n
0	19,700	272	36
0.5	19,300	275	35
1.0	18,800	277	34
2.0	18,600	277	33.8
3.0	17,400	275	31.6

*It is noted that the molecular weight decreases as the PA concentration goes up.

Table II. Summary of Saturation Moisture Contents of $PISO_2$ Specimen With Phthalic Anhydride End Caps*

PA Concentration (%)	MW (amu)	Saturation Moisture Content (w/o)
0	19,700	4.14±0.50
0.5	19,300	3.44±0.09
1.0	18,800	3.63±0.02
2.0	18,600	3.48±0.02
3.0	17,400	2.79±0.05

*It is noted that the saturation moisture content goes down with increasing PA end-cap concentration.

Table III. Summary of Long Component Lifetime (τ_2) and Intensity (I_2) Values in $PISO_2$ End-Capped With Phthalic Anhydride

End-Cap Concentration (%)	Molecular Weight (amu)	Long Component Characteristics			
		DRY		SATURATED	
		τ_2 (ps)	I_2 (%)	τ_2 (ps)	I_2 (%)
0	19,700	933±119	1.8±0.6	1161±110	1.2±0.2
3	17,400	933±69	1.7±0.2	944±171	1.8±0.7

Notes: (1) τ_2 and I_2 are independent of molecular weight in dry specimens.

(2) τ_2 decreases and I_2 increases with decreasing molecular weight (i.e., increasing PA concentration)in saturated specimens.

(3) The presence of PA-end caps appears to neutralize the effects of moisture on positron lifetime and intensity values.

It appears that the presence of phthalic anhydride end caps interferes with the normal entry of water into $PISO_2$ chain. In control specimens (0% end-cap concentration), water seems to be trapped at the amines resulting in decreased positronium formation and its subsequent decay. But the PA end-caps neutralize the amines leaving anhydride end-groups and free volume cells as the only places where water molecules can be trapped.

Table IV. Summary of Saturation Moisture Contents of $PISO_2$ End-Capped With Aniline

Aniline End-Cap Concentration (%)	Saturation Moisture Content (w/o)
0.0	4.14±0.5
2.0	3.05±0.05
3.0	3.23±0.11

Notes: (1) Aniline end-caps have significant effect on saturation moisture content of $PISO_2$ samples.

(2) There appears to be no decrease in saturation moisture content with increasing aniline concentration beyond 2%. (It is possible that the saturation moisture content stabilizes at aniline end-cap concentration of much less than 2 percent. See comments under Table V below.)

Table V. Summary of Saturation Moisture Contents of $PISO_2$ End-Capped With Aminobenzophenone (ABP)

ABP Concentration (%)	Saturation Moisture Content (w/o)
0.0	4.14±0.5
0.5	3.17±0.09
1.0	3.16±0.03
3.0	3.17±0.01

Notes: (1) ABP is similar to aniline in its effect on saturation moisture content of $PISO_2$ samples.

(2) The saturation moisture content of $PISO_2$ is independent of ABP concentration beyond 0.5%.

Table VI. Summary of Positron Annihilation Characteristics in $PISO_2$ Samples End-Capped With 3% of Phthalic Anhydride (PA), Aniline and Aminobenzophenone (ABP)

End Cap	Long Component Lifetime and Intensity			
	DRY		SATURATED	
	τ_2 (ps)	I_2 (%)	τ_2 (ps)	I_2 (%)
PA	933±69	1.7±0.2	944±98	1.8±0.7
Aniline	966±115	1.5±0.5	820±75	1.9±0.2
ABP	905±93	1.6±0.3	909±72	1.9±0.2

Apparently, all the end-caps have similar effects on positronium formation and annihilation characteristics in $PISO_2$ samples.

Table VII. Adhesive Properties of $PISO_2$ Samples as a Function of Phthalic Anhydride End-Cap Concentration

Phthalic Anhydride End-Cap Concentration (%)	Lap Shear Strength*, psi		Loss in Strength After Water Boil (%)
	Initial Value	Value After 72-Hour Water Boil	
0	4708	3306	30
0.5	3978	3442	14
2.0	3672	3280	11

*Each data point represents the average of four samples. Data variability was approximately ±10% from the average.

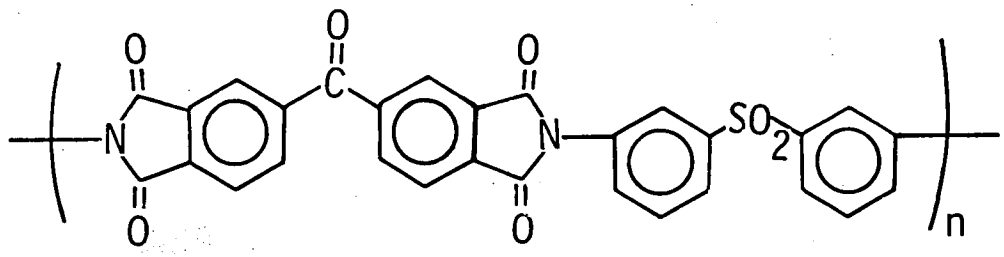

Figure-1. Chemical structure of Polyimidesulfone ($PISO_2$).

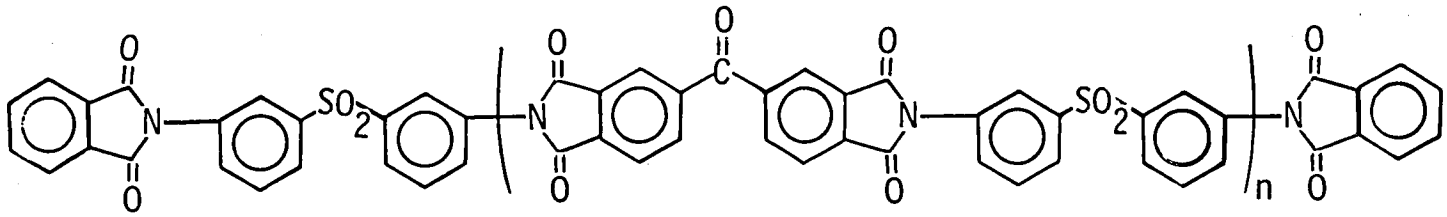

Figure-2. Chemical structure of Phthalic Anhydride-Endcapped $PISO_2$

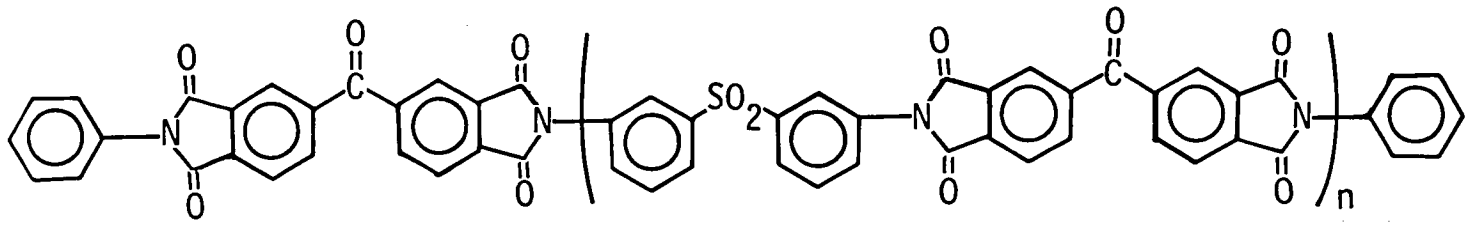

Figure-3. Chemical structure of Aniline-Endcapped $PISO_2$.

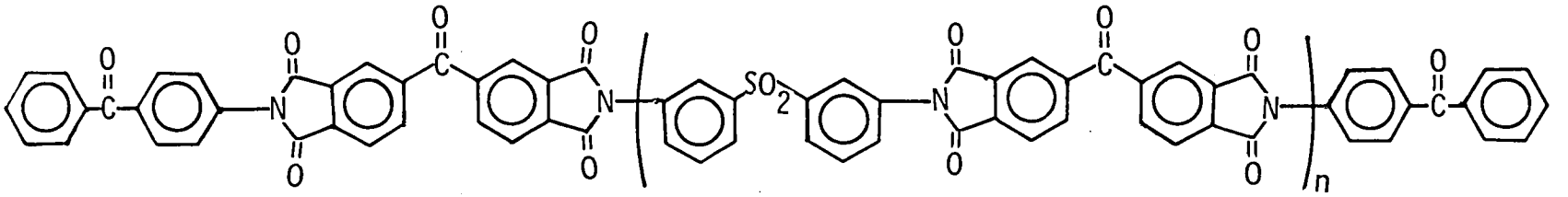

Figure-4. Chemical structure of 4-Aminobenzophenone-Endcapped PISO$_2$.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-86283		

4. Title and Subtitle	5. Report Date
A Study of the Effects of End-Cap Molecular Species on Environmental Characteristics of Polyimidesulfones	August 1984
	6. Performing Organization Code 505-33-90-01
7. Author(s) Jag J. Singh, Terry L. St. Clair, and Suzanne Walker*	8. Performing Organization Report No.
	10. Work Unit No.
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes

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16. Abstract

Polyimidesulfone ($PISO_2$) is a promising polymer developed at Langley. In a continuing effort to further improve its environmental stability and mechanical properties, we decided to investigate the effects of various types of end-caps on its thermo-mechanical and related properties. It is noted that end caps are effective in reducing the environmental damage susceptibility of $PISO_2$ samples, apparently due to their ability to react with free end groups which are believed to be moisture pickup sites. Phthalic anhydride, aniline and aminobenzophenone were the end caps used in this study.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Polyimidesulfone ($PISO_2$), End Caps, Phthalic Anhydride, Aniline, 4-Aminobenzophenone, Saturation Moisture Content, Adhesive Strength, Positron Annihilation	Unclassified - Unlimited Subject Category: 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	12	A02

For sale by the National Technical Information Service, Springfield, Virginia 22161